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Hierarchical Modelling of High-Molecular Weight Polymer Melts: From Soft Blobs to Microscopic Description

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We review recent progress in developing a hierarchical strategy for modelling homopolymer melts described with microscopic detail. The samples are gradually equilibrated at all length scales, proceeding from long to short wavelengths through sequential backmapping within a hierarchy of coarse-grained (CG) models. The models stem from the same generic concept, mapping macromolecules on chains of soft spheres (blobs). Each of them represents a microscopic subchain with $N_{\rm b}$ monomers and their bonded and non-bonded interactions are captured by simple force-fields. The hierarchy of CG models is obtained varying $N_{\rm b}$. Melts described with the lowest resolution soft-sphere model are generated by Monte Carlo simulations and are gradually fine-grained into representations of higher resolution. Once $N_{\rm b}$ becomes sufficiently small, millions of monomers underlying the soft-sphere melt can be reinserted through short Molecular Dynamics simulations, enabled by parallel computing. Chemically different melts can be grouped into classes according to the degree of overlap of their chains (quantified by the invariant degree of polymerisation). In spirit of Renormalisation Group procedures, we demonstrate that long-wavelength conformational and structural properties of an entire class can be captured through a single generic blob-based description. This "blueprint" has to be established only once and can be hierarchically backmapped to describe different materials within the same class. Focusing on method development, we employ for the microscopic description a generic bead-spring model, which retains key qualitative features of chemistry-specific models. Based on this description, it is demonstrated that the new techniques can straightforwardly equilibrate samples of unprecedented size, containing thousands of chains with degrees of polymerisation that are two orders of magnitude larger than the entanglement length. This achievement opens the way for future studies of molecular-scale mechanisms underlying polymer rheology.

1 Introduction

Understanding the connection between structure, processing, and properties of polymers with computer simulations, often requires their description with microscopic detail. This presents, however, a major challenge due to the broad spectrum[1–3] of characteristic length- and time-scales that are involved. For instance, polymer molecules are mesoscale objects with characteristic dimensions (e.g. radius of gyration) between 10 and 100 nm, formed by covalently linked monomers with sub-nanometre size. The time-scales associated with chain dynamics range from femtoseconds (bond vibrations) up to milliseconds or seconds (conformational relaxation of entire chains). To bridge the extremities of the scale-spectrum hierarchical modelling strategies are particularly attractive. The studied material is considered on several different levels of resolution, each described by an appropriate model. Above the atomistic level, coarse-grained (CG) models are implemented, representing a group of microscopic degrees of freedom by a single effective interaction centre.

The amount of decimated microscopic particles sets the resolution of the CG model. After the system is equilibrated with the coarser resolution, the degrees of freedom of the next level are reinserted and the configuration is re-equilibrated. The final reinsertion of chemical details may introduce millions of particles. Nevertheless computations remain tractable when parallelised, since fine-graining requires only local sampling.

Due to local relaxation of reinserted degrees of freedom, hierarchical approaches implicitly assume that the long-wavelength structure of the material is accurately reproduced on the crudest level of description. For many polymeric systems, this assumption can be rationalised by considering[3] hierarchical modelling strategies from the standpoint of renormalisation group (RG) method. For macromolecules, the RG approach was pioneered by de Gennes[4], who treated polymer chains on the basis of sequentially enlarged blocks of microscopic monomers. As the observation scale increases, these renormalisation transformations converge – irrespective of the underlying microscopic structure – to a generic description depending on a few characteristic parameters, also known as "invariants". In this scope, the universal long-wavelength behaviour can be captured by any model provided that it is projected on the same set of invariants.

Homopolymer melts are one of the simplest examples of polymeric materials. They are liquids of macromolecules derived from one species of monomer[5], presenting significant interest for industry (e.g. commodity polymers are processed in molten state) and basic polymer physics. For example, melts (alongside with solutions) provided a framework for the first, simple, mean-field-like descriptions of macromolecular behaviour[6]. These arguments lead to the astonishing conclusion (Flory theorem) that in melts excluded volume intra- and inter-molecular interactions compensate each other. Hence, on large scales chain conformations follow the statistics of an ideal random walk. The scaling law $R_\mathrm{e}^2 = Nb_\mathrm{e}^2$, is one of the hallmarks of this statistics, where R_e^2 is the mean-square end-to-end distance of the molecule, N the polymerisation degree, and b_e^2 a chemistry-specific coefficient. Hence the number of polymer molecules threading through the volume spanned by a test chain is proportional to $\sqrt{\bar{N}} \equiv \rho R_\mathrm{e}^3/N \sim \sqrt{N}$, where ρ is the monomer number density. $\bar{N}$ is the invariant degree of polymerisation, playing a central role in polymer theory. Corrections to Flory's theorem[7,8], demonstrate that the behaviour of simple polymeric systems can be surprisingly complex even for static properties.

The interpretation of dynamics and rheology of molten homopolymers is more challenging. Many of the underlying processes are understood only in the limit of linear response, on the basis of tube theories[9–13] presenting a mean-field-like approach to polymer dynamics. The collective dynamics of polymer molecules is reduced to the problem of single-chain motion in a transient tube, representing topological constraints (entanglements) imposed on chain dynamics by surrounding chains. *Provided* that large, equilibrated samples of long homopolymer melts described with atomistic resolution are available, tube theories offer a framework for predicting macroscopic linear rheological behaviour from the underlying microscopic picture. For example, the plateau modulus can be determined[9] as $G_N^0 = (4/5)\rho k_\mathrm{B}T/N_\mathrm{e}$. The average number of monomers, N_e, between two consecutive topological constraints (entanglement length) can be obtained via, e.g. primitive path analysis[14]. For nonlinear viscoelasticity, extensions of the tube model[9,13,15] can account for some experimental observations. The agreement, however, is by far not perfect[16,17] and understanding nonlinear viscoelasticity remains an open field of research.

Here, we summarise a novel hierarchical strategy[18,19] which enables the study of struc-

tural, dynamical, and rheological properties by equilibrating melts of unprecedented size and chain-length, described with microscopic detail. The approach represents homopolymer chains as strings of soft spheres[20,21] (blobs), each of them corresponding to a subchain of $N_{\rm b}$ monomers. The quantity of microscopic monomers "lumped" into each sphere sets the resolution at the given level of the hierarchy. In addition, it determines the degree of sphere/sphere overlap (the "softness" of CG interactions) since the amount of interdigitating $N_{\rm b}$-monomer subchains scales as $\sqrt{N_{\rm b}}$. Fine-graining is performed within the sequence of these soft models and microscopic details are efficiently reinserted using high-performance parallel computing, once the resolution becomes sufficiently high. Notably[19], for different homopolymers with the same $\bar{N}$ the hierarchy of CG models at crudest resolutions converges to a universal representation, allowing the generation of their equilibrated configurations from a single long-wavelength "blueprint".

The manuscript is organised as follows. Sec. 2 presents a generic microscopic model for homopolymer melts. Sec. 3 introduces the soft-sphere model. Sec. 4 presents the backmapping strategy placed in Sec. 5 in context of universal representations of homopolymer melts. Sec. 6 provides a short summary.

2 Generic Microscopic Model

Focusing on method development, we employ for the microscopic description of polymer melts a generic bead-spring model[22], incorporating microscopic features that are crucial for reproducing qualitatively the behaviour of real-life molten polymers, especially regarding dynamics and rheology. These features include hard excluded volume, strong covalent bonds, and high density.

Homopolymer melts are modelled as ensembles of $n_{(\gamma)}$ linear chains, composed of $N_{(\gamma)}$ monomers linked by finitely extensible nonlinear elastic (FENE) springs. Chain stiffness is controlled through a standard angular potential[23]. Non-bonded interactions are captured through the repulsive Weeks-Chandler-Andersen (WCA) potential. By varying the number density of the monomers, $\rho_{(\gamma)}$, and the strength of the angular potential, $\kappa_{\theta(\gamma)}$, the model can mimic chemical diversity. The subscript γ denotes homopolymer "type", i.e. two homopolymers are of different types if their molecules are unlike in some respect. A standard parameterisation of the model is employed[22], while all lengths and energies are expressed in units of the characteristic WCA length-scale and thermal energy, k_BT.

Moderately-sized melts are equilibrated with more conventional techniques to provide reference data for parameterising the soft-sphere model and validating hierarchical fine-graining. We implement a configuration-assembly procedure[23,24], operating directly on the microscopic scale. Chains with conformations drawn from the distribution expected in the melt are treated as rigid bodies and arranged relaxing excluded volume constraints. Random placement of molecules generates high density fluctuations, leading[23,24] to significant conformational distortions when recovering excluded volume. Thus the molecular arrangement is optimised through a Monte Carlo (MC) scheme[23,24]. Then excluded volume can be reintroduced through a slow "push-off", employing[23] force-capped WCA potentials. During the "push-off", realised using Molecular Dynamics (MD), chain-deformation is minimised adjusting force capping through a feedback loop[24].

Recent studies demonstrated[24] that the computational time of the MC optimisation, increases significantly with chain length. Thus, although state-of-art configuration-assembly

procedures can relax large melts of entangled polymers[24], in practice they are more suitable for samples with medium-sized chains, $N_{(\gamma)} \sim 500$. Postulating conformational properties constitutes a more fundamental limitation, since their estimation is challenging in melts with non-linear molecules and inhomogeneous systems.

3 Drastically Coarse-Grained Blob-Based Models

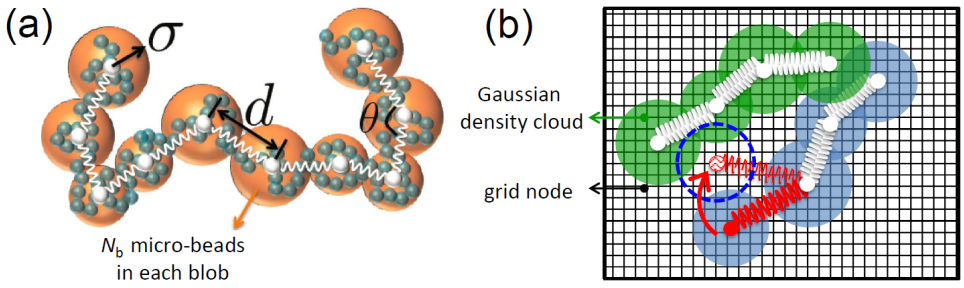

Figure 1. a) Polymer molecule described with microscopic detail (blue) represented[20,21] by a chain of spheres (yellow) with fluctuating radii. b) Two-dimensional cartoon illustrating the three-dimensional method[21], assigning the Gaussian density clouds of the spheres to the nodes of a lattice. For clarity only two chains are shown with different colours. Total densities at each node are obtained summing the contributions from all density clouds and employed to calculate the total energy due to non-bonded interactions. During a MC move (red arrow), one needs to calculate changes in local densities only at nodes affected by the move, without neighbour lists.

A CG representation with adjustable resolution is obtained by mapping microscopic polymer molecules on chains of soft spheres, as illustrated in Fig. 1a. The radius σ and the coordinates of the centre of a sphere, match the instantaneous gyration radius and centre-of-mass (COM) of the underlying $N_{\rm b}$-monomer subchain. Each CG chain contains $N_{\rm CG}$ blobs linked by simple harmonic bond and angular potentials[20,21,25]. Fluctuations of σ are controlled[20,21] by a combination of potentials proposed by Lhuillier[26] and Flory[27]. Non-bonded interactions between two spheres are given by a Gaussian potential, corresponding to an overlap of two Gaussian density clouds. Each of them approximates the distribution in space of $N_{\rm b}$ monomers underlying the two spheres.

The CG model can be treated with standard MC or MD techniques. However, computational efficiency can be hampered by the large number of interacting neighbours, increasing as $\sim \sqrt{N_{\rm b}}$. To avoid neighbour-lists, the non-bonded energy can be *equivalently rewritten*[21] as a functional $\mathcal{H}_{\rm nb} \sim \int d\mathbf{r}(\phi^2(\mathbf{r}) - \psi^2(\mathbf{r}))$. The collective variables $\phi(\mathbf{r})$ and $\psi(\mathbf{r})$ are expressed through the Gaussian density clouds of the spheres. The functional is discretised introducing a fine mesh. As illustrated in Fig. 1b, at each grid node the collective variables are calculated from the contributions of all clouds. Thus an MC scheme[21] can be employed, where energy differences entering the Metropolis criterion are calculated from the changes induced by a MC move to the collective variables on the "lattice background", avoiding an explicit consideration of pairwise interactions.

To parameterise the soft-sphere model, in reference samples $N_{\rm b}$-monomer subchains are identified to calculate quantifiers of *local* conformations and liquid structure. Typi-

cal examples are[18] distributions of gyration radii of subchains, distance between COMs of sequential subchains, and angles between vectors connecting COMs of sequential subchains. The parameters then follow from standard structure-based coarse-graining[1–3] with these quantifiers as an input. After parameterisation, the soft-sphere model can accurately reproduce[18] remaining structural and conformational properties.

4 Backmapping Strategy

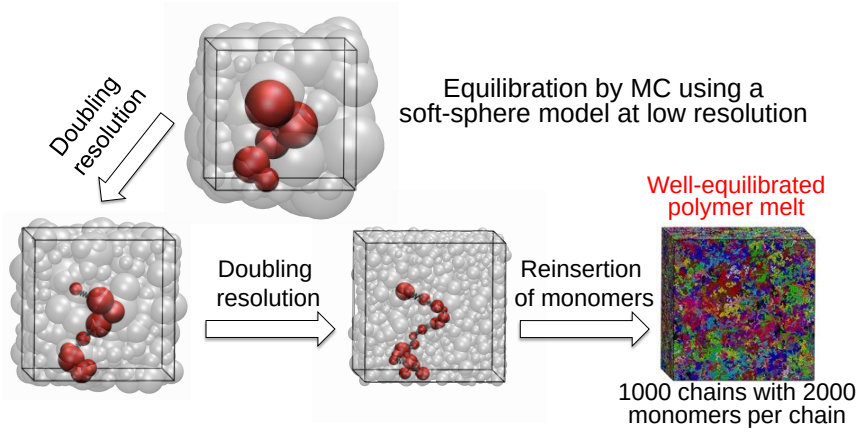

Figure 2. Sketch of the hierarchical backmapping strategy. The last snapshot on the right presents an equilibrated microscopic melt (colours are randomly chosen to improve visibility of different chains). Adapted from Ref. 18.

The sequential backmapping strategy[18] for creating large samples of high molecular weight polymers is summarised in Fig. 2. Initially a CG melt is equilibrated, each sphere representing a large number of microscopic beads. These configurations are sequentially fine-grained, doubling at every step the resolution. The procedure involves only motion of dumbells, characterised by short relaxation time. The configurations after the last fine-graining step are employed to recover the full microscopic description. Each soft-sphere polymer is replaced by a microscopic bead-spring chain in a matching conformation without non-bonded interactions. This configuration, is subjected to a "push-off" procedure[23,24] and short re-equilibration. Provided that the melt of the soft-sphere chains, into which the microscopic details are reinserted, corresponds to $N_\mathrm{b} < N_\mathrm{e}$ the "push-off" and relaxation require only short MD simulations[18].

Most steps of hierarchical backmapping are inexpensive computationally. Parallel computations are involved only during "push-off" and re-equilibration. Typical CPU-time demands are illustrated considering $N_{(\gamma)} = 2000$ melts with thousand chains equilibrated in less than three days, when employing 32 processors during reinsertion of microscopic details[18]. Equilibrating the same systems with configuration-assembly on 32 processors lasts more than ten days, even when utilising the efficient ESPResSo++ package[28].

Fig. 3 illustrates the equilibration of backmapped samples, comparing structural and conformational properties with their counterparts in a reference melt. It follows from

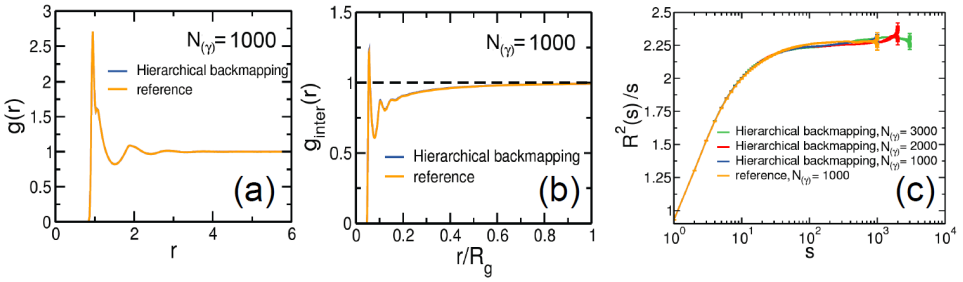

Figure 3. a) Pair-distribution function, $g(r)$, calculated in backmapped (blue line) and reference (orange line) melts ($\kappa_{\theta(\gamma)} = 1$ and $\rho_{(\gamma)} = 0.85$) with $N_{(\gamma)} = 1000$. b) Same as left panel but for the intermolecular part of the pair-distribution function, $g_{\rm inter}(r)$. c) Internal distance plot, $R^2(s)/s$, calculated in backmapped melts for three different chain lengths $N_{(\gamma)} = 1000$, 2000, and 3000 (blue, red, and green lines) and reference systems (orange line) with $N_{(\gamma)} = 1000$. Similar comparison has been reported in Ref. 18.

Fig. 3a that in backmapped melts the pair-distribution function, $g(r)$, is indistinguishable from the reference data, demonstrating the correct description of microscopic liquid structure. Fig. 3b compares the intermolecular part of the pair-distribution function, $g_{\rm inter}(r)$, in the same melts against reference data. The match of the curves confirms that the packing of the polymer chains (correlation hole) is also reproduced. The agreement between polymer conformations in backmapped and reference melts is demonstrated in Fig. 3c by the internal distance plot, $R^2(s)/s$. Here $R^2(s)$ is the mean square distance of intramolecular monomers and s is the difference of their ranking numbers along chain backbone. Within the noise of the data, the curves match very well, which is a significant achievement due to the sensitivity of the internal distance plot to potential distortions of chain shape [18,23].

5 Universal Long-Wavelength Description of Homopolymer Melts

Coarse-graining polymer melts into ensembles of chains of soft-spheres is similar to a RG procedure. For homopolymer melts with the same $\bar{N}_{(\gamma)}$ (denoted as "class") this process converges[19], increasing $N_{\rm b}$, to a universal long-wavelength representation – an analog of a "fixed point". For each melt in the same class, this universal long-wavelength representation can be defined introducing a coarse-graining length scale[29], $\Delta L_{(\gamma)}$, renormalising the microscopic coordinate space as $\tilde{\mathbf{r}} = \mathbf{r}/\Delta L_{(\gamma)}$. The shortest subchains that are resolved after this coarse-graining operation contain an amount of monomers, $N_{b(\gamma)}$, such that their characteristic size equals $\Delta L_{(\gamma)}$. Thus, (cf. Fig. 4) in the renormalised space all homopolymers are represented as melts of chains of blobs, with the same average diameter equal to unity. In the renormalised blob representation the statistics of the a) distance between the COMs of two sequential blobs and b) angle between two vectors joining the COM of a blob with the COMs of the preceding and the succeeding blob, are universal[19,25]. Therefore the conformations of CG chains in all homopolymers will be the same, provided that they are represented by the same number of blobs N_{CG}. The last requirement can be fulfilled by matching[19] their coarse-graining scales. In addition, the melts will have the same liquid structure in renormalised space. This follows, first observing[19] that for same N_{CG} the melts will have an identical degree of polymerisation, $\bar{N}_{b(\gamma)}$, also on the level of

subchains. The connection between mesoscale liquid structure of polymers and invariant degree of polymerisation was predicted by de Gennes[4]. Considering the packing of polymer molecules he demonstrated that the chain density within the volume of a test chain is reduced by a universal factor $1-\bar{N}_{(\gamma)}^{-1/2}$ (Fig. 3b presents this correlation hole). Similarly, liquid packing of subchains depends in a universal way[30] on $\bar{N}_{b(\gamma)}$.

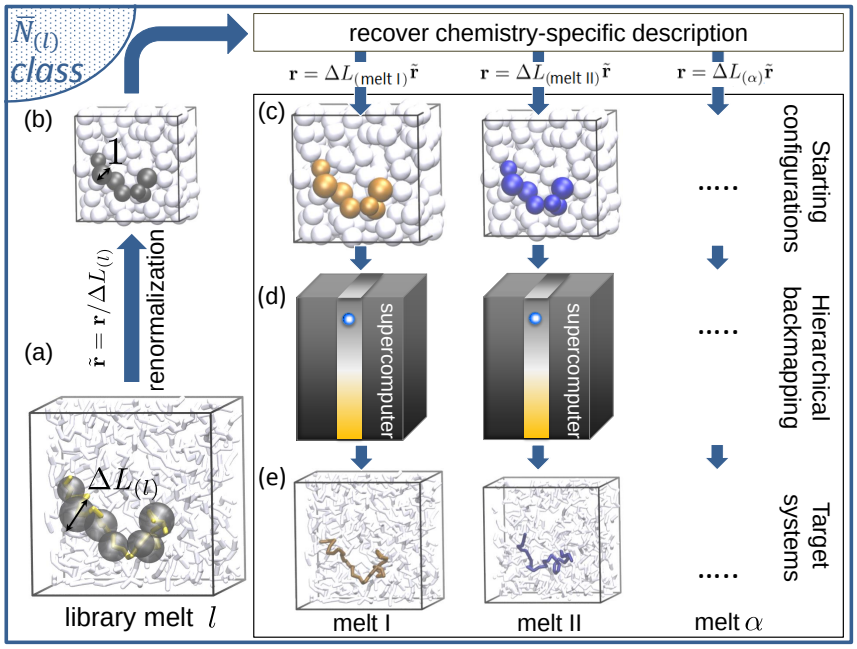

Figure 4. Hierarchical modelling scheme for homopolymer melts with the same invariant degree of polymerisation, $\bar{N}_{(l)}$. a) A library sample described with microscopic detail is subjected to coarse-graining (the average blob size is $\Delta L_{(l)}$) and renormalisation of coordinate-space, $\tilde{\mathbf{r}}=\mathbf{r}/\Delta L_{(l)}$, to obtain b) a universal blob-based blueprint of long-wavelength structure. c) The blueprint is projected on the coordinate space of any other target α-type melt of the same class, back-transforming as $\mathbf{r}=\Delta L_{(\alpha)}\tilde{\mathbf{r}}$. The scales $\Delta L_{(l)}$ and $\Delta L_{(\alpha)}$ are properly matched to ensure the same amount of blobs. d) The blob-based description serves as an input for hierarchical backmapping, delivering e) equilibrated α-type melts described with microscopic detail. Adapted from Ref. 19.

These arguments rely on ideal random walk statistics of polymer conformations predicted by the Flory theorem. The latter was corrected[7,8], demonstrating that the volume spanned by a chain exhibits a hierarchy of nested correlation holes of all possible subchains. This introduces weak self-avoidance leading to deviations from the ideal random walk statistics. These deviations, however, diminish increasing N_{b} and for our practical purposes can be neglected after a certain threshold. The latter can be established monitoring $R^2_{b(\gamma)}/N_{b(\gamma)}b^2_{\mathrm{e}(\gamma)}$ as a function of $N_{b(\gamma)}$ in reference samples.

The above suggest that homopolymer melts within the same class can be interconverted via the common blob-based description, simplifying their hierarchical equilibration. Namely, one needs to generate the universal CG representation only once, preferably on the basis of the simplest microscopic model with the desired $\bar{N}_{(\gamma)}$. For example, "materials

genomic" libraries can be developed, containing for each invariant degree of polymerisation a few morphologies which can be easily coarse-grained to define the blob-based "blueprint". As outlined in Fig. 4, microscopic representations of any class-member can be recovered reinserting chemical details into this common description via the hierarchical backmapping approach[18].

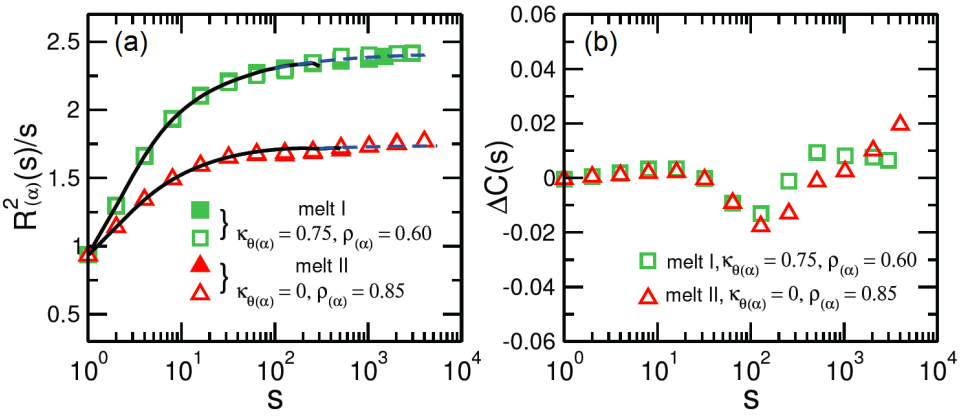

Figure 5. a) Symbols present the internal distance plot, $R^2_{(\alpha)}(s)/s$, for melts I and II equilibrated by backmapping the universal long-wavelength description. Solid lines present $R^2_{(\alpha)}(s)/s$ calculated from reference simulations of shorter melts, extrapolated to larger s (blue dashed lines) on the basis of theoretical predictions[7,8]. b) Relative deviation, $\Delta C(s)$, of internal distance plots in backmapped melts I and II for $\bar{N}_{(\alpha)} = 15 \times 10^3$ from their counterparts in reference samples. Adapted from Ref. 19.

The feasibility of this approach is illustrated[19] considering library samples characterised by $\kappa_{\theta(l)} = 1.5$ and $\rho_{(l)} = 0.85$, covering a broad range of invariant degrees of polymerisation $7.5 \times 10^3 \leq \bar{N}_{(l)} \leq 15 \times 10^3$ which are representative of values encountered in experiments. The library melts were equilibrated through the hierarchical backmapping procedure[18] of Sec. 4. Configurations of all other systems can be obtained by hierarchically backmapping the blob-based blueprint generated from one of these library melts with the same $\bar{N}_{(l)}$. As an example, we discuss two chemically different systems with $\kappa_{\theta(\alpha)} = 0.75$, $\rho_{(\alpha)} = 0.60$ (melt I) and $\kappa_{\theta(\alpha)} = 0$, $\rho_{(\alpha)} = 0.85$ (melt II). For $N_{(\text{melt I})} = 1500$ and $N_{(\text{melt II})} = 2000$ both melts map on $\bar{N}_{(l_1)} = 7.5 \times 10^3$ while for $N_{(\text{melt I})} = 3000$ and $N_{(\text{melt II})} = 4000$ they correspond to $\bar{N}_{(l_2)} = 15 \times 10^3$.

Fig. 5a demonstrates equilibration of melts I and II backmapped from the universal blueprint, presenting their internal distance plots, $R^2_{(\alpha)}(s)/s$, which follow closely their counterparts in *independent* reference simulations. Fig. 5b quantifies the deviation of the plots for $\bar{N}_{(\gamma)} = 15 \times 10^3$, through their relative difference $\Delta C(s) = [C_{(\alpha)} - C_{(\text{ref})}]/C_{(\text{ref})}$. Here $C_{(\alpha)}$ are the internal distance plots in melt I and II while $C_{(\text{ref})}$ is their counterpart in reference samples. It can be observed that the relative difference is at most 2%. Comparing pair correlation functions in backmapped and reference melts confirms[19] that liquid structure is also correctly reproduced.

6 Concluding Remarks and Outlook

We demonstrated that melts of high molecular weight homopolymers can be efficiently equilibrated employing a novel hierarchical strategy. The method combines low resolution blob-based models capturing accurately long-wavelength properties and fine-graining techniques, allowing for gradual reinsertion of decimated degrees of freedom. Parallel computing is essential for the last stage of fine-graining where *short-time* sampling of configurational space is required by millions of reinserted microscopic particles. Above certain scales, the blob-based models provide a universal description of an entire class of melts, corresponding to homopolymers with the same invariant degree of polymerisation. This blueprint can be hierarchically backmapped to equilibrate any other class-member. Although a generic bead-spring model was chosen for the microscopic description, we expect that similar backmapping strategies can be developed for chemistry-specific models.

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